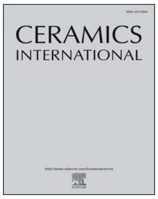
Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint



Effects of PTFE activation and carbon sources on combustion synthesis of Cr_2AlC/Al_2O_3 composites

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ARTICLE INFO

Keywords:
B. Composites
D. Carbides
Cr_2AlC
Combustion synthesis
PTFE

ABSTRACT

Formation of Cr_2AlC/Al_2O_3 in situ composites was investigated by self-propagating high-temperature synthesis (SHS) involving both PTFE activation and aluminothermic reduction. In addition to Al and Cr_2O_3 as the starting materials, carbon black, graphite, and Al_4C_3 were used as the carbon sources. PTFE was employed not only as a reaction promoter, but also as a carburizing agent. Depending on different sources of carbon, the threshold amounts of PTFE for inducing self-sustaining combustion were 1.5, 4.0, and 3.0 wt% for the samples adopting carbon black, graphite, and Al_4C_3, respectively. The combustion front velocity and temperature increased with increasing PTFE content. Moreover, the sample using carbon black was the most exothermic, while the Al_4C_3-based sample was the least. For the powder compacts adopting carbon black or graphite, Cr_2AlC/Al_2O_3 composites were produced with no impurities. Due to relatively weak reaction exothermicity, however, the synthesized composites containing small amounts of Cr_7C_3 and Al_4C_3 were obtained from the Al_4C_3-based reaction scheme.

1. Introduction

The MAX phases are a class of hexagonal-structure ternary compounds, which possess a unique combination of metallic and ceramic properties owing to their inherently laminated crystal structure where the M–X bond has a mixed covalent/ionic character, while the M–A bond is metallic [1–3]. Their composition is formulated by $M_{n+1}AX_n$ (n = 1, 2, or 3), where M is an early transition metal, A is an A-group (mostly IIIA or IVA) element, and X is either C or N [1]. In general, the MAX phases have low density, high stiffness, high thermal conductivity, and good oxidation and corrosion resistance at high temperatures, as carbides and nitrides; while they are relatively soft, readily machinable, electrically conductive, resistant to thermal shock, and highly tolerable to damage, as metals [4–7]. Moreover, some MAX carbides, such as Ti_2AlC, Ta_2AlC, Cr_2AlC, and Ti_3AlC_2, have demonstrated high-temperature crack healing behavior, which is a result of the filling of cracks by a well-adhering Al_2O_3 layer at two opposing crack faces [8–10].

Among MAX phases, Cr_2AlC is particularly attractive due to its remarkable mechanical properties [11], excellent high-temperature oxidation and corrosion resistance [6], and crack healing capability [9]. Reactive hot pressing [6,12–15] and pulse discharge sintering (PDS) or spark plasma sintering (SPS) [11,16–18] have been commonly used to prepare Cr_2AlC. With an in-situ hot pressing/solid-liquid reaction method, Lin et al. [6,12] produced Cr_2AlC from the mixture of Cr, Al, and graphite powders and proposed a set of reaction mechanisms involving two intermetallic compounds, Cr_2Al and Cr_5Al_8. Tian et al. [13,14] indicated the need of excess Al to reduce the impurity Cr_7C_3 when Cr_2AlC was produced from Cr, Al, and graphite powders by hot pressing at 850–1450 °C under 20 MPa for 1 h. As reported by Li et al. [15], two intermediate phases (Cr_2Al and $Cr_{23}Al_6$) disappeared and single-phase Cr_2AlC was obtained from a mechanically activated powder mixture composed of Cr:Al:C = 2:1.2:1 under a hot pressing temperature of 1100 °C. By means of the PDS method at 1250 °C, Cr_7C_3 and Cr_2Al were found in the as-synthesized Cr_2AlC from the Cr–Al–C and Cr–Al_4C_3–C reaction systems, respectively [11,16]. According to Oh et al. [17], Cr_2AlC with a small amount of Cr_2Al was fabricated by SPS from the Cr–Al–C mixture at 1200 °C while high-purity Cr_2AlC was obtained from the Cr–Al–Cr_3C_2 mixture at 1100 °C. Most of the previous studies on the preparation of Cr_2AlC pointed out the existence of Cr_7C_3 and/or Cr_2Al as the impurities in the end product [11–19]. However, the presence of Cr_7C_3 reduced the fracture toughness, thermal expansion coefficient, thermal conductivity, specific heat capacity, and electrical conductivity of Cr_2AlC [20,21].

Recent investigations have indicated that fracture toughness, flexural strength, and hardness of the MAX carbides are improved by incorporating a second ceramic phase, for example TiB_2, TiC, and Al_2O_3 [22–25]. Besides, the addition of SiC fibers into the Cr_2AlC matrix was shown to increase the wear resistance by 70–80% [26]. On account of

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http://dx.doi.org/10.1016/j.ceramint.2017.09.187
Received 25 August 2017; Received in revised form 19 September 2017; Accepted 22 September 2017

Please cite this article as: Yeh, C.L., Ceramics International (2017), http://dx.doi.org/10.1016/j.ceramint.2017.09.187

the high hardness, high modulus, excellent chemical stability and comparable thermal expansion coefficient, Al_2O_3 has been considered as an effective reinforcement for Cr_2AlC. Fabrication of Cr_2AlC/Al_2O_3 in situ composites from the mixture of Cr_3C_2, Cr, Al, and Cr_2O_3 powders was conducted by reactive hot pressing at 1400 °C under 16 MPa for 2 h [25]. The reaction of Al with Cr_2O_3 produced Al_2O_3 and Al_8Cr_5, both of which were consecutively involved in the interaction with Cr_3C_2, Cr, and Al to form Cr_2AlC [25].

As a promising alternative, combustion synthesis in the mode of self-propagating high-temperature synthesis (SHS) takes advantage of the self-sustaining merit from highly exothermic reactions, and hence, has the benefits of low energy requirement, short reaction time, high-purity products, and simple facilities [27,28]. On the formation of the MAX phases, the SHS technique has been applied to prepare Ti_3SiC_2, Ti_3AlC_2, Ti_2AlC, and Ta_2AlC from the elemental powder compacts [29–31]. Moreover, the SHS method involving aluminothermic reduction of metal oxides has been shown to be an in situ processing route capable of producing Al_2O_3-reinforced MAX carbides [32–34]. However, formation of Cr_2AlC from its constituent elements by SHS is unfeasible, due to insufficient reaction exothermicity. With the aid of the reaction enthalpy released from aluminothermic reduction of Cr_2O_3 and preheating temperature up to 300 °C, self-sustaining combustion of was achieved in the Cr_2O_3–Al–Al_4C_3 powder compact and the resulting product was a Cr_2AlC/Al_2O_3 composite with Cr_7C_3 as the impurity [34]. Excess Al was found to reduce the content of Cr_7C_3 but an extra amount of Al_4C_3 had almost no effect on the decrease of Cr_7C_3 because probably of a decline in the combustion temperature with increasing Al_4C_3 [34].

This study made a novel attempt to prepare the Cr_2AlC/Al_2O_3 composite by means of a chemically-activated SHS method with PTFE (polytetrafluoroethylene or Teflon) as the activator. The roles played by PTFE are twofold: to promote the SHS reaction and to act as a carburizing agent. Moreover, three carbon sources, including carbon black, graphite, and Al_4C_3, were adopted to blend with Cr_2O_3 and Al as the starting materials. Effects of PTFE activation and different types of carbon were investigated on combustion sustainability, combustion wave velocity and temperature, and formation of Cr_2AlC.

2. Experimental methods of approach

The starting materials employed by this study included chromium (III) oxide (Cr_2O_3, Showa Chemical Co., < 45 µm, 99% purity), aluminum (Strem Chemicals, < 45 µm, 99.7% purity), carbon black (Showa Chemical Co., 20–40 nm, 99% purity), graphite (Aldrich Chemical, < 45 µm, 99% purity), aluminum carbide (Al_4C_3, Strem Chemicals, < 45 µm, 98% purity), and PTFE ($-(C_2F_4)_n-$, Alfa Aesar Co., 6–10 µm). For the powder mixtures adopting carbon black (C_b) and graphite (C_g), their corresponding stoichiometries are formulated as Reactions (1) and (2). The sample composition of the Al_4C_3-based scheme is expressed in Reaction (3).

$$Cr_2O_3 + 3Al + (1-x)C_b + xC_{PTFE} \xrightarrow{-(C_2F_4)_n-} Cr_2AlC + Al_2O_3 \quad (1)$$

$$Cr_2O_3 + 3Al + (1-y)C_g + yC_{PTFE} \xrightarrow{-(C_2F_4)_n-} Cr_2AlC + Al_2O_3 \quad (2)$$

$$Cr_2O_3 + \left(\frac{5+4z}{3}\right)Al + \left(\frac{1-z}{3}\right)Al_4C_3 + zC_{PTFE} \xrightarrow{-(C_2F_4)_n-} Cr_2AlC + Al_2O_3 \quad (3)$$

where C_{PTFE} represents carbon supplied from complete decomposition of PTFE. The coefficients, x, y, and z, signify the mole fraction of C_{PTFE} in the total carbon.

The amount of PTFE in the range of 1.0–6.0 wt% was added into the reactant mixture. As a reaction promoter, PTFE is able to peel off the Al_2O_3 shell on the surface of the Al particle and enhances the reactivity of Al powders [35,36]. As a carburizing agent, PTFE generates carbon (C_{PTFE}) through thermal decomposition and C_{PTFE} participates directly in the reaction [37]. It was found that based upon the above three reaction systems, combustion ceased to propagate and quenched after ignition for the PTFE-free samples. Experimental observations indicate that the threshold amounts of PTFE required for inducing self-sustaining combustion in Reactions (1), (2), and (3) are 1.5, 4.0, and 3.0 wt% respectively. These threshold values are correspondingly equivalent to $x = 0.07$, $y = 0.20$, and $z = 0.15$ in Reactions (1), (2), and (3).

Compared with 1.5 wt% PTFE required by the sample of Reaction (1), a larger amount of PTFE (4.0 wt%) had to be added into the graphite-containing sample of Reaction (2). This is partly because the particle size of carbon black is much smaller than that of graphite. As a result, the sample of Reaction (1) has a higher degree of reactivity stemming from a larger surface area of carbon black powders to contact with other reagents. Partly, this is caused by the fact that the thermal conductivity of graphite is larger than that of carbon black, which resulting in more heat lost by conduction from the combustion front and hence a lower reaction temperature for the graphite-adopted sample [29]. As far as the Al_4C_3-based reaction scheme is concerned, the need of a higher threshold of 3.0 wt% PTFE could be a consequence of the samples containing a lesser amount of Al compared to Reaction (1).

The reactant powders were dry mixed in a ball mill and then cold-pressed into cylindrical test specimens with a diameter of 7 mm, a height of 12 mm, and a compaction density relative to 60% of the theoretical density. The SHS experiment was conducted in a windowed stainless-steel chamber under an atmosphere of high purity argon (99.99%). No prior heating was applied on the PTFE-activated sample compacts and the ignition of the sample was accomplished by a heated tungsten coil with a voltage of 60 V and a current of 1.5 A. The SHS process was recorded by a color CCD video camera (Pulnix TMC-7). The combustion wave velocity was determined from the time sequence of recorded images. The combustion temperature was measured by a fine-wire (125 µm) Pt/Pt-13%Rh thermocouple attached on the sample surface. Phase constituents of the final product were identified by an X-ray diffractometer (Bruker D2) with CuK_α radiation. The product microstructure was examined under a scanning electron microscope (Hitachi S3000N). Details of the experimental methods were previously reported [38].

3. Results and discussion

3.1. Self-propagating combustion characteristics

Fig. 1(a) and (b) presents two recorded SHS sequences illustrating typical combustion behavior observed by this study. For the 1.5 wt% PTFE-activated sample of Reaction (1), as shown in Fig. 1(a), shortly after ignition the combustion front forms a localized reaction zone moving along a spiral path over the sample surface. It took about $t = 5.87$ s for the spinning combustion wave to spread from the ignition plane to the bottom of the sample. Moreover, the flame spreading process left visible corkscrew marks on the sample surface. The spinning combustion behavior is considered as unstable propagation of the combustion wave, because the heat flux liberated from self-sustaining combustion is inadequate to maintain a planar reaction front propagating steadily. There are thermodynamic and kinetic reasons which provide the basis for departure from the steady condition [39]. Thermodynamic considerations arise from the degree of reaction exothermicity. Kinetic reasons are largely attributed to insufficient reactivity on account of the presence of diffusion barriers. The role of PTFE was to alleviate these two limitations and to stimulate the synthesis reaction.

Fig. 1(b) displays the combustion sequence of a graphite-adopted sample of Reaction (2) with 4 wt% PTFE. Because of the addition of a larger amount of PTFE, a broader and faster reaction zone was established and a shorter flame spreading period of about $t = 4.73$ s was reached. Besides, axial elongation of the burned samples was observed in Fig. 1(a) and (b). There are two mechanisms responsible for this phenomenon. One is due to the growth of plate-like Cr_2AlC grains into a